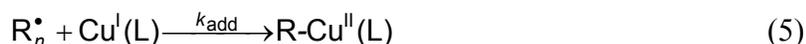


## Measurement of Cu<sup>II</sup>-Mediated ATRP Deactivation and Cu<sup>I</sup>-Mediated Organometallic Reactions via SP-PLP-EPR in Butyl Acrylate Polymerization

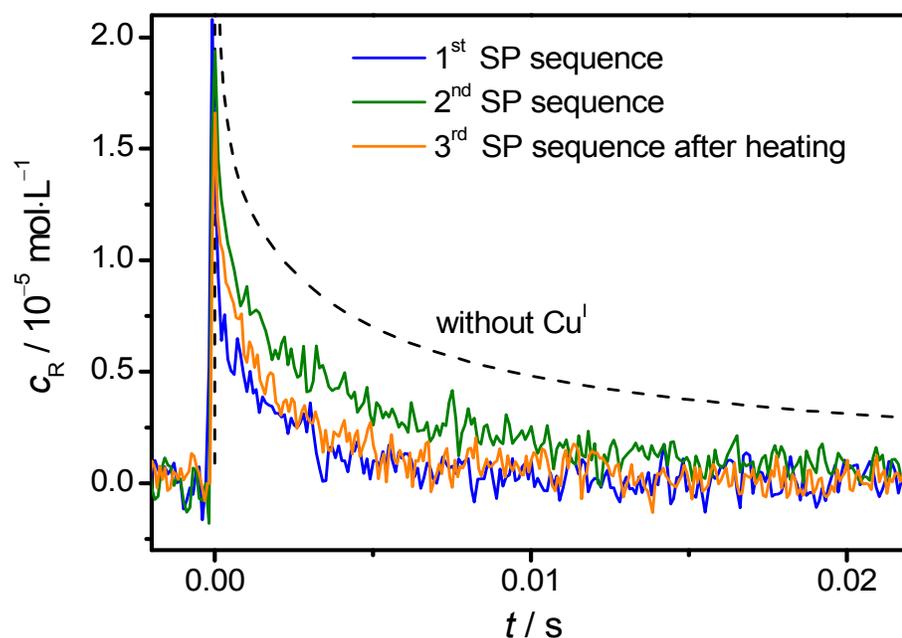
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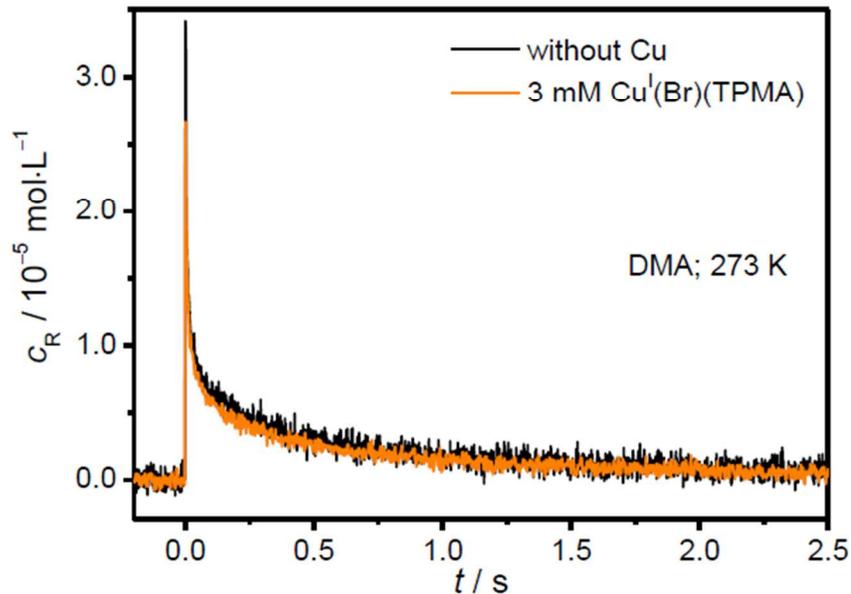
**Scheme S1:** Reaction scheme used for PREDICI<sup>®</sup> modeling of the  $c_R$  vs time traces of SP-PLP-EPR experiments.  $k_{p,1}$  (Eq. 1) was assumed to be  $100 \times k_p$ .  $k_p$  (eq 2) and  $k_t$  (eq 3) were taken from literature. Termination was included via the composite model for chain-length-dependent  $k_t$ .<sup>1</sup> Equation 4 was included for modeling the  $c_R$  vs time data of the experiment with Cu<sup>II</sup> to deduce the associated rate coefficient  $k_{deact}$ . Similarly, eq 5 was used instead of eq 4 for modeling the  $c_R$  vs time data of the experiment with Cu<sup>I</sup> to deduce  $k_{add}$ .

## EPR Experiments with Cu<sup>I</sup>

For the EPR investigations illustrated in Figure 4, a solution of [Cu<sup>I</sup>(TPMA)]Br and of the photoinitiator  $\alpha$ -methyl-4-(methylmercapto)- $\alpha$ -morpholinopropiophenone (MMMP) in MeCN/BA was prepared. The mixture contained the Cu<sup>I</sup> ATRP catalyst. Due to the absence of the ATRP initiator, RBr, no formation of the [Br-Cu<sup>II</sup>(TPMA)]Br ATRP species via halogen transfer could occur. Therefore, radicals were not generated by ATRP activation, but by laser-induced decomposition of the photoinitiator. In analogous experiments, described in ref. <sup>2</sup>, [Cu<sup>I</sup>(TPMA)]PF<sub>6</sub> was used instead of [Cu<sup>I</sup>(TPMA)]Br to avoid the presence of a halogen counter ion. It was verified that the formation of an organometallic complex with the primary radicals of the photoinitiator plays no role.<sup>2</sup> The experiments were carried out at -40 °C with a sequence of laser pulses being applied, as detailed in the main text.



**Figure S1:** Radical concentration,  $c_R$ , vs time traces recorded at  $-40\text{ }^\circ\text{C}$  during BA polymerizations with the laser single pulse (SP) being applied at time zero. The first SP sequence (blue line) was recorded in the presence of  $1\text{ mM } [\text{Cu}^{\text{I}}(\text{TPMA})]\text{Br}$ . The decay in  $c_R$  vs time is much faster than in the absence of  $\text{Cu}^{\text{I}}$  (dashed black line) due to the reaction of the  $\text{Cu}^{\text{I}}$  complex with propagating radicals as detailed in the main text. The second SP sequence (green line) was recorded after having applied around 100 SPs without EPR detection to convert part of the  $\text{Cu}^{\text{I}}$  species to the stable  $\text{R-Cu}^{\text{II}}$  intermediate as evidenced in Figure 4 of the main text. Due to the lowering of  $\text{Cu}^{\text{I}}$  concentration, the decrease in the subsequently recorded  $c_R$  vs time trace is slower than in the first sequence. The third SP sequence (orange line) was recorded at  $-40\text{ }^\circ\text{C}$  after heating the sample to  $20\text{ }^\circ\text{C}$  for 2 minutes. The decay in  $c_R$  vs time is again as fast as in the initial sequence, which confirms that the heating process resulted in the regeneration of  $\text{Cu}^{\text{I}}$  from  $\text{R-Cu}^{\text{II}}$  as explained in the main text.



**Figure S2:** Time-resolved radical concentration vs time curves from EPR experiments on DMA polymerized in solution with 15 wt% MeCN at 0 °C. The black line refers to the experiment in the absence of Cu, whereas the orange line is recorded in the presence of 3 mM  $[\text{Cu}^{\text{I}}(\text{TPMA})]\text{Br}$ . Despite the considerable amount of  $\text{Cu}^{\text{I}}$ , the two traces are not significantly different. It may be concluded that the decay of  $c_{\text{R}}$  vs time is due to radical–radical termination without any significant contribution from  $\text{Cu}^{\text{I}}$ -mediated organometallic reactions as opposed to the analogous experiment with butyl acrylate detailed in the main text.

#### References:

- (1) Smith, G. B.; Russell, G. T.; Heuts, J. P. A. *Macromol. Theory Simul.* **2003**, *12*, 299–314.
- (2) Wang, Y.; Soerensen, N.; Zhong, M. J.; Schroeder, H.; Buback, M.; Matyjaszewski, K. *Macromolecules* **2013**, *46*, 683–691.